THE REDUCTION OF ORGANIC COMPOUNDS IN LIQUID AMMONIA-SODIUM SOLUTIONS.

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INTRODUCTION.

The alkali metals and the metals of the alkaline earths are very strong reducing agents at ordinary temperatures but their use in reduction has been very much limited because of lack of a suitable solvent. When reactions are carried out with sodium as in the Fittig and Wurtz methods, the substance used was dissolved in an inactive solvent. In such a mixture, the reaction is confined to the surface contact between metal and solution and hence the rate of reaction is very slow.

Sodium in liquid ammonia is a strong and fairly convenient reducing agent and may also be used for the Wurtz condensation. One advantage of the method is that at this low temperature organic compounds are very stable.

The reduction of organic compounds in liquid ammonia with metallic sodium is of comparatively recent date. In 1864, Weyl published in the "Annales de Poggendorff" the results of his experiments on the solution of the alkali metals in liquid ammonia. Gore published in the "Philosophical Magazine" for 1872, volume 44, page 315, the results of his work. He dissolved, or attempted to dissolve, some 250 compounds and elements in liquid ammonia and then treated them with sodium. Apparently his only observations were that no free carbon was liberated.

The first work specifically on the reduction of organic compounds in liquid ammonis with sodium and other

alkali metals was done by Chablay[1] at the University of Paris and this work was published in book form in 1913. The nature and extent of his work makes it necessary to give it some attention in this paper.

Chablay's first work was the action of sodium on the alkyl chlorides in liquid ammonia and, also, on other alkyl halides. His experiments showed that sodium in liquid ammonia reacted with the alkyl halides for the formation of the hydrocarbon and the alkyl amine according to the following reaction:

$$2CH_3I + 2Na + 2NH_3 = CH_4 + CH_3NH_2 + 2NaI + NH_3$$

For the higher members of the series such as ethyl, propyl, butyl and the higher alkyl halides, the percentage of hydrocarbon increases and the percentage of alkyl amine decreases as we go up the series. In some cases, we may also get the formation of the unsaturated compounds as ethylene, propylene, etc.

The dichlorides, such as ethylene and propylene chlorides, yielded the unsaturated compounds in a manner analagous to KOH.

$$C_3H_6Br_2 + 2NH_3 + 2Na = C_3H_6 + 2NaBr + 2NH_3$$

Chablay also prepared the alcoholates of the various alkali metals and the sodium derivatives of various amides.

Probably the most complete investigations of the reduction of organic compounds in liquid ammonia has been done under the direction of Kraus. The following work was

done by Kraus and White[2].

Hydrocarbons: With few exceptions, sodium is without action on the hydrocarbons. In tertiary hydrocarbons with large groups, the hydrogen of the tertiary carbon is often replacable with sodium. For example, triphenyl methane reacts as follows:

$$(C_6H_5)_3CH + Na = (C_6H_5)_3CNa + 1/2H_2$$

Alcohols: The alcohols react readily with sodium in liquid ammonia for the formation of the alcoholates. The alcoholates are not reduced by the sodium - a fact which may be due to their sparing solubility in ammonia.

Phenols: Phenols react readily with sodium and the phenolates are much more soluble than the alcoholates.

Thiophenols: Thiophenols differ from the phenols in that they react with the solvent forming the ammonium salt. This ammonium salt reacts with sodium for the formation of the sodium salt.

$$C_6H_5SNH_4 + Na = C_6H_5SNa + NH_3 + 1/2H_2$$

Ethers: The ethers appear to be stable and are not acted upon by sodium in liquid ammonia.

Aldehydes: Aldehydes or the addition products of aldehydes and ammonia are acted upon by sodium. Acetaldehyde ammonia with sodium in liquid ammonia yielded a compound of the composition CH_3ONaNH_2. On the addition of water and subsequent distillation, a solution which gave all the tests for acetaldehyde was obtained.

Acetone: Acetone is soluble in ammonia and sodium will react with such a solution rapidly but quietly. Fumes of a camphor-like odor were given off. On the addition of water and subsequent evaporation, the liquid separated into two layers of sodium hydroxide and acetone. Evidently sodium forms an addition product with acetone and ammonia which is decomposed on the addition of water.

Benzophenone: Sodium acts on benzophenone in the ratio of two atoms of sodium to one of benzophenone. The residue after distillation of the ammonia was a black crystalline powder which hycholyzed in water with an odor of benzophenone.

Sodium Acetate: Sodium acetate dissolves in liquid ammonia but remains unchanged after the addition of sodium.

Propyl Iodide: Propyl iodide dissolved in ammonia and sodium added gave largely propane and some propyl amine.

Tertiary Amyl Iodide: On treatment with sodium and ammonia, secondary pentane is formed.

Ethylene Chloride: Ethylene chloride reacts rapidly with sodium in liquid ammonia to yield ethylene.

$$C_2H_4Cl_2 + 2Na = C_2H_4 + 2NaCl$$

Acetylene Dibromide: If sodium be added to acetylene dibromide in liquid ammonia, a gas with a garlic like odor is evolved which gives a precipitate when passed into ammoniacal cuprous chloride solution. The residue and an

odor of acetylene and was soluble in water and this aqueous solution gave a precipitate with cuprous chloride indicating acetylene.

The reaction probably proceeds according to the following equations:

$$C_2H_2Br_2 + 2Na = 2NaBr + C_2H_2$$

$$C_2H_2Br_2 + 4Na = 2NaBr + C_2Na_2 + H_2$$

$$C_2H_2 + 2Na = Na_2C_2 + H_2$$

Benzyl chloride: Benzyl chloride reacts readily with sodium in liquid ammonia forming a white precipitate and a pink colored solution. The nature of the products was not determined.

Phenyl Halides: The phenyl halides react with sodium in liquid ammonia with considerable violence. About one atom of sodium is required for one molecule of the halide. The chief products are diphenyl and triphenyl amines and benzene.

Ortho-Chloro-Toluene: To sodium dissolved in ammonia ortho-chlor toluene was added until the color changed from blue to red. On evaporation of the ammonia, a syrupy liquid was left behind which, on separation and distillation, boiled at 100 - 125° and was evidently toluene. The residue seemed to be ortho-toluidine.

The reaction then appears to go as follows:

$$2CH_3C_6H_4Cl + 2Na + NH_3 = C_6H_5CH_3 + CH_3C_6H_4NH_2 + 2NaCl$$

Para-chlor toluene reacted in a manner analagous to that

of the ortho compound yielding toluene and para-toluidine.

Dichlorobenzene: Ortho-dichlorobenzene reacts vigorously with sodium in ammonia. From the mixture was isolated some ortho-phenylenediamine. Some benzene was also formed in the reaction which probably goes as follows:

$$2C_6H_4Cl_2 + 4Na + 2NH_3 = C_6H_6 + C_2H_4(NH_2)_2 + 4NaCl$$

Alpha-Bromnapthalene: Sodium reacts vigorously with alpha bromnapthalene. After evaporation of the ammonia crystals of napthalene sublimed when the tube containing the mixture was heated.

Nitro Benzene: Nitrobenzene with sodium in liquid ammonia yielded aniline, azoxy benzene, azobenzene and hydrazo benzene. These will be discussed later.

Phenyl Mustard Oil: Phenyl mustard oil on treatment with sodium yields no benzene. The oily residue remaining after distillation of the ammonia was treated with water yielded aniline and a few crystals of diphenyl.

Benzanilide: Benzanilide was treated with sodium but without any definite results.

Sodium Benzene Sulfate: This compound reacts rapidly and quietly with sodium forming a yellow precipitate. It appears to require two atoms of sodium to one atom of sodium benzenesulfonate. The residue, after removal of ammonia, yielded about 70% of the theoretical amount of benzene possible.

Phenyl Sulfide: Phenyl sulfide reacts with sodium in liquid ammonia. A small amount of benzene was isolated

from the mixture but nothing else was determined. This experiment indicates the instability of the thio ethers as compared to aliphatic oxygen ethers.

George F. White[3] further investigated the reaction between sodium and chlorbenzene in liquid ammonia in an attempt to prepare sodium phenyl. No evidence of the formation of the compound was obtained. The principle products of the reaction are benzene, diphenyl amine, triphenyl amine and sodium halide.

The sodium reacts with the aryl halide in the ratio of one atom of the former to one molecule of the latter, as shown in the following equations:

$$6C_6H_5Cl + 6Na + NH_3 = 3C_6H_6 + (C_6H_5)_3N + 6NaCl$$

$$4C_6H_5Cl + 4Na + NH_3 = 2C_6H_6 + (C_6H_5)_2NH + 4NaCl$$

In the presence of excess sodium, the diphenyl amine is partially converted into sodium diphenyl amide and any aniline formed is converted into sodium anilide. Chlor benzene yields about 75% of benzene.

White and Knight[4] did some further work on the reduction of nitrobenzene and its reduction products in liquid ammonia. Nitro benzene is a good representative of a large class of substances and a knowledge of its action would be helpful in predicting the reduction products of related compounds. Nitro benzene is soluble in ammonia and hence very convenient to use. Reduction takes place readily. Various sodium derivatives and reduction pro-

ducts have been prepared with sodium in non aqueous solvents such as boiling toluene containing chlor nitro benzene.

The reaction of sodium in liquid ammonia on nitro benzene appears to go as follows:

$$C_6H_5NO_2 + 4Na + NH_3 = C_6H_5N(Na)ONa + NaNH_2 + NaOH$$

In the addition of water to the reaction mixture, azobenzene and azoxybenzene were isolated. By using ammonium chloride, the disodium salt is converted into its corresponding ammono acid in the absence of water.

$$C_6H_5NNaONa + 2NH_4Cl = C_6H_5NHOH + 2NaCl + 2NH_3$$

Then in liquid ammonia, reduction of nitro benzene proceeds as in all other solvents, phenyhydroxyl amine being the first product to be isolated and nitroso benzene may be assumed to be an intermediate product since indirect methods have indicated its formation in aqueous solutions. Azo bodies are not formed primarily but may result from secondary reactions in aqueous alkaline solutions.

Nitro benzene when treated with an excess of sodium in liquid ammonia forms the disodium anilide which by the action of ammonium chloride or water yields aniline.

Solutions of nitro benzene in liquid ammonia are very little colored if the nitrobenzene is pure and freshly distilled. The color, however, is usually violet or red. As sodium was added, the solution first became yellow, followed by orange, red and finally a dark brown. The reaction

was rapid but not violent. In the presence of large excesses of sodium explosions were apt to occur. On partial reduction of nitrobenzene and evaporation of the ammonia, exposure to the air resulted in violent explosions[#] accompanied by flame and deposition of carbon. Formation of disodium phenyl hydroxylamine. Sodium was added to nitro benzene in liquid ammonia in the ratio of four atoms of sodium to one of nitro benzene. Ammonium chloride was then added and the mixture stirred. This decomposes all sodium compounds. The resulting mixture had a yellow color and yielded beta phenylhydroxylamine.

Nitro benzene reduced with six atoms of sodium to one of the nitro benzene and allowed to stand twenty-four hours. A brownish gree solution resulted from which, on treating with water, aniline separated.

The formation of sodium amide was shown as follows: Nitro benzene was reduced with sodium and alpha bromnapthalene was added. Water was added, the ammonia evaporated and the mixture made acid with hydrochloric acid. This was extracted with ether to remove azoxy benzene and the brown napthalene and the mixture was then made alkaline. Alpha-napthylamine crystallized from the solution. It was probably formed according to the following equation:

$$C_{10}H_7Br + NaNH_2 = NaBr + C_{10}H_7NH_2$$

If sodium is added to nitro benzene in the propor-

[#]See page 21

tion necessary to reduce it only to the azo and azoxy benzene, these compounds will be formed when water is added to the reduction mixture.

Nitroso benzene on reduction yielded phenylhydroxyl amine. Phenyl hydroxyl-amine on reduction yields aniline. Azoxybenzene reduces to azo benzene, hydrazo benzene and finally aniline. If hydrazo benzene be treated with sodium and ethyl iodide, mono-ethyl aniline is formed.

Triphenyl methyl appears to be a compound in which carbon is tri-valent. One molecule of tri-phenyl chlor methane reacts with two atoms of sodium to form one molecule of sodium chloride and a compound of sodium and triphenyl methyl.

$$(C_6H_5)_3CCl + 2Na = (C_6H_5)_3CNa + NaCl$$

This sodium compound is very reactive and, with water, forms sodium hydroxide and triphenyl methane.

Triphenyl methane reacts with sodium slowly to form sodium triphenyl methyl and hydrogen. If sodium tri phenyl methyl is present in liquid ammonia solution, we would expect it to react with tri phenyl methyl chloride.

$$(C_6H_5)_3CNa + (C_6H_5)_3CCl = 2(C_6H_5)_3C + NaCl$$

If equivalent quantities of sodium and tri-phenyl chlormethane in liquid ammonia has an equivalent quantity of triphenyl chlormethane added together with some toluene for a solvent the yellow color characteristic of triphenyl me-

thyl appears.

Dry air was passed through the solution and the white amorphous precipitate formed was washed and crystallized from benzene and proved to be the peroxide of triphenyl methyl.

Tetra phenyl methane is easily prepared by the action of brom benzene on sodium triphenyl methyl. The reaction is more rapid if toluene is used as a solvent.

Solutions of triphenyl methyl chloride in liquid ammonia conduct the electric current as do also solutions of sodium triphenyl methyl.

The fact that benzaldehyde reacts with sodium has been known for some time. Church[5] studied a benzaldehyde sodium addition product and reported that it was decomposed by water for the formation of benzyl alcohol and benzaldehyde.

It is assumed by F. F. Blicke[6] that benzaldehyde and sodium react with the formation of a mono or a di-sodium addition product depending on the amount of sodium present.

$$C_6H_5\text{-}C\begin{matrix}H\\O\end{matrix} + Na = C_6H_5\text{-}C\begin{matrix}H\\ONa\end{matrix} = Na = C_6H_5\text{-}C\begin{matrix}H\\ONa\end{matrix} - Na$$

This mono sodium derivative may react with benzaldehyde to form benzyl alcohol. The addition of an atomic weight of sodium to one molecular equivalent of benzaldehyde results in a mixture of compounds. The following have been isolated; benzyl alcohol, hydrobenzoin, benzoin, benzyl benzoate, benzyl ether and benzoic acid.

With two atoms of sodium benzaldehyde yields benzyl

alcohol. These reactions were carried out in ether.

Many organic compounds containing hydroxyl[7], sulfhydroxyl, amino or imino groups in their molecules have an acid function in liquid ammonia and form salts in that solvent with the alkali metals or in some cases preferably with the alkali metal amides. Such salts may react with certain organic halides, the hydrocarbon radical of the latter replacing the metal atom of the salt. The object of the present investigations was to study the general character of these reactions.

The reactions between the salts and the halides after proceeding quantitatively where their is no action between the halide and liquid ammonia. It is sometimes difficult where there is such a small amount of material to isolate the entire product.

The reactions which occur at -33° are usually complete in five minutes or less. They approach the ionic type of reaction whereas similar syntheses in different media require much higher temperatures and many hours to go to completion.

Ethyl alcohol and sodium do not react in the exact proportion of one molecule of alcohol to one atom of sodium in liquid ammonia, a white precipitate being formed and an excess of sodium left in the solution. A compound of the composition $C_2H_5ONa.C_2H_5OH$ is probably formed. Ethyl ether was prepared by adding to potassium ethylate

made by the action of potassium amide on alcohol.

Ethyl-n-Butyl Ether: Potassium amide treated with ethyl alcohol and normal butyl bromide gave a 20% yield of ethyl butyl ether. Normal butyl ether could not be synthesized by this method.

Ethylene Glycol Ethers: Glycol is soluble in ammonia and reacts quantitatively with sodium with the evolution of hydrogen and the formation of the white insoluble monosodium glycolate. It reacted slowly with ethyl iodide for the formation of glycol monoethyl ether.

Ethyl-Benzyl Ether: To a solution in liquid ammonia of potassium alcoholate was added some benzyl chloride. A white precipitate formed and an 80% yield of ethyl-benzyl ether was obtained.

Benzyl Ether: Using potassium, benzyl alcohol and benzyl chloride, a 55% yield of benzyl ether was obtained.

Sodium Phenolate: Phenol dissolved in ammonia reacts with sodium for the formation of sodium phenolate.

Anisole: A solution of phenol in ammonia was treated with sodium and gaseous methyl chloride was then passed into the mixture. A 42% yield of anisole was obtained.

Phenetole: Phenol was dissolved in ammonia, sodium added and finally ethyl bromide was added. A 60% yield of phenetale was obtained.

Reduction of alpha Napthol: To alpha napthol suspended in liquid ammonia, one molecular equivalent of sodium was added. The following reaction appeared to take

place:

$$4C_{10}H_7OH + 4Na = 3C_{10}H_7ONa + C_{10}H_{16}ONa$$

the napthol being partially reduced to tetra-hydro napthol. Beta napthol yielded the analogous beta compound.

Resorcinol mono ethyl ether and diethyl ether were prepared in an analogous way.

Thiophenolates: Thio phenol reacts with ammonia to form ammonium thiophenolate which is soluble in liquid ammonia. On the addition of sodium, sodium thiophenolate is formed.

Ethyl-Phenyl Thio Ether: Thio phenol, sodium and ethyl bromide yielded 80% of the theoretical amount of ethylphenyl thio-ether.

Ethyl Acetamide: Potassium was converted into amide and acetamide was added followed by ethyl bromide. A 34% yield of ethyl acetamide was obtained.

Monoethyl aniline, ethyl diphenyl amine, ethyl acetanilide and ethyl pthalimide were prepared in an analogous manner.

Probably the latest work on the reduction of organic compounds in liquid ammonia was done by Schlubach and Miedel[8] and published in the Berichte for October, 1924. This work differed from previous work in that ammonium chloride was added to the liquid ammonia previous to the addition of sodium. The course of the reduction process was followed by determining the changes in the index of

refraction which allowed a quantitative estimation of the reduction to be made.

The reduction of double bonds differs for the various types of compounds. The ethylene double bond is reduced when it is in the alpha position to a phenyl group. Phenyl butylene is reduced to phenyl butane. Cinnamic acid and stilbene remain unchanged.

The carbonyl double bond is more easily reduced. Benzophenone is reduced directly to diphenyl methane without difficulty. Michlers ketone, di-biphenyl ketone, benzil, benzoin and desoxy-benzoin are unchanged. Acetophenone is not easily reduced to phenyl isobutyl alcohol. Benzal acetone reduces to phenyl isobutyl alcohol.

The reductions were carried out by mixing the substance with an excess of ammonium chloride and passing in ammonia while the container was cooled to -70° and the sodium added. In the case of insoluble substances, the container was well shaken and a solvent, ether or benzene, was added. At the end of the reaction, water is added and the organic substances extracted with ether.

1-Phenyl Butylene: The phenyl butylene was dissolved in ether as it was insoluble in ammonia and ammonium chloride and sodium added. The index of refraction became less and corresponded to a reduction of 93% of the original substance to butyl benzol.

Benzophenone: Benzophenone was easily reduced to diphenyl methane.

Benzyl acetone: The reduction of benzyl acetone goes very easily to phenyl butanol.

Benzal acetone is less easily reduced than benzyl acetone as it is not very soluble in ammonia. The reduction product is phenyl butanol.

Pyridine: Pyridine is easily soluble in ammonia and easily reduces to piperidin.

The above contains a fairly complete summary of the work which has been done on the reduction of organic compounds in liquid ammonia with sodium. Briefly, it consisted of (1) action of sodium in liquid ammonia on organic halides for the formation of ethers, etc; (2) the beginning of a systematic study of the reduction of general types of organic compounds by Kraus and his colleagues; (3) the work done in Germany by Schlnbach and Miedel using ammonium chloride together with ammonia and sodium. It is the latter work which the present research most nearly resembles.

In the following work, no attempt was made to systematically choose any particular general class of compounds or to choose examples from the principle groups of compounds. The compounds which we reduced or attempted to reduce were simply chosen at random.

GENERAL PROCEDURE.

In this work, the reductions were carried out in open Dewar bulbs of 250 c.c. capacity. No attempt was made to exclude air or moisture from the reaction mixture.

The amount of substance reduced was governed by the amount of sodium necessary for the reduction. The limit for the amount of sodium to be added to one Dewar bulb was approximately ten grams. Any larger quantity resulted in precipitate so heavy as to make efficient stirring impossible. For most of the substances, the amount used was ten grams requiring from four to eight grams of sodium and approximately twice this amount of ammonium chloride.

Ammonium chloride was added to the ammonia before the addition of sodium, in quantity great enough to be equivalent to the sodium added. This, in effect, gave an acid solution of liquid ammonia.

Insolubility of some compounds in liquid ammonia offered some difficulties. Either very vigorous stirring or solvents had to be resorted to.

Due to the nature of the apparatus, no good mechanical method of stirring was convenient. Hence, in the case of substances insoluble in ammonia, a solvent was resorted to. Ether, benzene and toluene were tried on the compounds which were insoluble and providing the compound was soluble in ether, this solvent was used in preference to the others.

Even with soluble compounds, however, good stirring

aided materially in the efficient and rapid reduction of the compound in question. Stirring by hand was efficient but tiresome and, at best, could only be done intermittently especially when several reductions were being carried out at the same time. A very simple and good method of stirring was finally used. The sodium to be added was cut into slices from one to two centimeters in area and one to two millimeters in thickness. By holding these against the inside of the Dewar and pressing a glass rod against the flat surface of the sodium, the sodium would stick with more or less tenacity to the rod. Then, by sliding the sodium along the side of the Dewar to the bottom, it would be held their by the weight of the glass rod until the sodium was almost completely used up and at the same time would stir the solution vigorously and efficiently.

Separation of the products of the reduction from the sodium chloride, ammonium chloride, sodium hydroxide and unchanged substance offered some difficulty which differed with the various compounds.

Where the substances formed in the reaction were insoluble in water, addition of water and filtration or separation in a funnel was used. Extraction of the reaction mixture with ether or some other solvent works in some cases. Where the compounds formed were soluble in water other means had to be used.

Purification and identification of the resulting pro-

ducts of reduction was usually not difficult. The simple nature of the compounds formed made identification fairly simple.

EXPERIMENTAL.

Alkyl and Aryl Cyanides.

In the work of Dains, Vaughn and Janney[9] on the determination of cyanides in organic compounds with liquid ammonia and sodium, they reported that probably a portion of the cyanide was converted into the amine. Some of the cyanide is split off of the compound undergoing reduction and it would be possible for the remainder to be converted into the amine. The following equations indicate what might take place.

$$RCN + 2Na = R - R + 2NaCN$$

$$RCN + 4Na + 4NH_3 = RCH_2NH_2 + 4NaNH_2$$

A sample of CH_3CN, C_6H_5CN, $C_6H_5CH_2CN$, C_3H_7CN and $CNCH_2COOC_2H_5$ were weighed into separate Dewars containing some 50 c.c. of liquid ammonia. An excess of sodium was added and the solution became permanently blue. The ammonia was allowed to evaporate and alcohol was added to decompose any remaining sodium. The mixture was dissolved in water and filtered. The solution was made acid with hydrochloric acid and the unchanged cyanide extracted with ether. The remaining solution was evaporated to dryness on the water bath and the residue of ammonium chloride, sodium cyanide and amine hydrochloride, if present, extracted with absolute alcohol. The absolute alcohol solution was evaporated to dryness and a very small residue consisted of ammonium chloride only.

At times, a faint odor suggestive of amines was noticeable but none could be recovered from the reaction mixture. In all cases, cyanide was split from the compound RCN for the formation of sodium cyanide, the larger percentage of cyanide being split from the compound in the case of the $C_6H_5.CH_2CN$ and the least in the case of C_6H_5CN.

The above was repeated with C_6H_5CN using ammonium chloride but practically all the compound was recovered unchanged and without any indication of amine formation.

Azo-Benzene.

Ten grams of azo benzene was placed in liquid ammonia in which it was only slightly soluble. An excess of sodium was added and the mixture allowed to stand until the ammonia was evaporated. On the addition of a small amount of alcohol or water, a sharp explosion occured.# This was probably due to the formation of some sodium compound formed with the azo benzene. Dr. Brewster had noted a similar, but more violent explosion with nitrobenzene. Work along this line was then discontinued since Kraus and his associates had already worked out this reaction and have succeeded in preparing hydrazo benzene and other reduction products of azo-benzene.

#See page 9.

Acetone

Acetone reacts with sodium for the formation of various condensation products, if the reaction is carried out at normal temperatures. Thinking that perhaps at the low temperature of liquid ammonia these condensation products might not be formed and instead isopropyl alcohol might be the product of the reaction, the reduction of acetone was attempted. If such was the case, the reaction would proceed according to the following equation.

$$CH_3COCH_3 + 2Na + 2NH_3 = CH_3CHOHCH_3 + 2NaNH_2$$

To twenty-five cubic centimeters of acetone in liquid ammonia was added 15 grams of sodium. The mixture was allowed to stand until the ammonia was evaporated and water was added. A black oil separated. This oil was distilled on the water bath and the first fraction boiling from 70° to 85° was collected and appeared to be unchanged acetone. The next fraction was a yellow oil boining from 85° to 112° and had a camphor-like odor and was probably a mixture of mesityl oxide and pinacoline. The final fraction boiled from 112° to 200° and consisted probably of acetoneamines and pinacone. No isopropyl alcohol was isolated as a product of the reaction. Apparently, the only reactions which take place are the well known condensation reactions which take place at ordinary temperatures.

This same reaction was repeated using ammonium chloride dissolved in the ammonia but no isopropyl alcohol was

obtained.

The acetone appears to form some sort of an addition product# with the sodium which separates as an oil and disappears on making the solution acid. The reaction between the sodium and acetone proceeds rapidly but quietly.

Nitro Benzene.

Nitro benzene dissolves readily in liquid ammonia with a colorless to deep violet color depending upon the purity of the nitro benzene. Sodium acts upon this solution quietly but vigorously with a gradual disappearance of the color, the solution being white. After addition of the total amount of sodium necessary to react completely with the nitro benzene. Complete reduction of the nitro benzene would proceed according to the following equation:

$$C_6H_5NO_2 + 6Na + 6NH_4Cl + 6NH_3 =$$

$$C_6H_5NH_2 + 6NaCl + 12NH_3 + 2H_2O.$$

To 150 c.c. of liquid ammonia containing 13 grams of ammonium chloride was added five grams of nitro-benzene. To this mixture, six grams of sodium was added. After evaporation of the ammonia water was added and this solution filtered. The filtrate was extracted with ether and the ether solution separated. On evaporation of the ether, a yellow oil remained.

This oil gave a violet color with bleaching powder, formed a salt with hydrochloric acid and with benzoyl chloride gave salt which melted at 160°. With acetyl

#See page 4.

chloride the oil formed a compound which melted at 114°. From these facts, the oil was evidently aniline.

From five grams of nitrobenzene was obtained three grams of aniline out of a possible 3.7 grams or approximately 80% of the theoretical amount.

Other experiments were tried using amounts of sodium corresponding to two atoms of sodium per atom of nitrobenzene and again with four atoms of sodium per atom of nitrobenzene but only proportionately small amounts of aniline were obtained. No other intermediate products of the reduction of nitrobenzene were obtained.

This is in accordance with the fact that in acid solution nitro benzene yields aniline.

Para-Nitro Toluene.

Para-nitro toluene is only slightly soluble in ammonia, hence in order to get an efficient reduction ether was used as a solvent for the nitro-toluene. This solution had a color resembling that of the nitro benzene. Sodium reacts with the solution rapidly and vigorously, the solution being white at the end of the reduction. Complete reduction of the para-toluidine would proceed according to the following equation:

$$6CH_3 - C_6H_4 - NO_2 + 6Na + 6NH_4Cl + 6NH_3 =$$
$$CH_3C_6H_4NH_2 + 6NaCl + 12NH_3 + 2H_2O$$

To five grams of para nitro toluene dissolved in ether and the whole dissolved in liquid ammonia containing eleven grams of ammonium chloride, five grams of sodium was added.

After addition of all the sodium, the solution was white in color and contained a white precipitate. The ammonia was evaporated and water was added to the mixture. This solution was extracted with ether and the ether was evaporated leaving a brown crystalline substance which melted at 43°.

The crystals formed a salt with hydrochloric acid and in acetyl chloride, a crystalline compound melting at 151°. From these data the compound was evidently para-toluidine.

From five grams of nitro toluene was obtained 3.5 gms. of para toluidine or slightly more than a 90% yield. Evidently in acid (NH_4Cl) solution, para-nitro toluene is completely reduced to para toluidine.

If less than the necessary amount of ammonium chloride to react with the added sodium is used, the solution becomes alkaline. If reduction of para-nitro toluene takes place in such a solution, the solution becomes red and then yellow. If reduction is stopped when the solution is yellow in color, the ammonia evaporated and water added, the remaining undissolved precipitate consists of azo-toluene. In one such case, three grams of azo toluene, melting point 141° (144°) was obtained from five grams of para-nitro toluene. In another run, a yellow crystalline compound was obtained which melted at 100° and was probably a mixture of azo- and hydrazo toluene. These results parallel those of

Kraus and his co-workers on nitro benzene and its reduction products.

Then in alkaline solution, para-nitro toluene yields azo and hydrazo toluene and in acid solution yields para toluidine.

$$2CH_3C_6H_4NO_2 + 8Na + 8NH_3 + 4NH_4Cl =$$
$$CH_3C_6H_4N - N - C_6H_4CH_3 + 4NaOH + 4NaCl + 12NH_3.$$

$$2CH_3C_6H_4NO_2 + 10Na + 10NH_3 + 6NH_4Cl =$$
$$CH_3C_6H_4NH - NH - C_6H_4CH_3 + 4NaOH + 10NaCl + 16NH_3.$$

The reactions may probably occur in the manner shown in the above equations. Instead of performing the reduction in ammonia without any NH_4Cl whatever, it might possibly result in a better yield to use the proportions according to the above equations.

Alpha-Nitro Naphthalene.

Alpha nitro-napthalene is difficultly soluble in liquid ammonia and not very soluble in ether. Toluene was tried as a solvent but the toluene carrying the dissolved nitro naphthalene sank to the bottom of the Dewar and did not make a good mixture with the ammonia. After a number of trials, ether was selected as the best solvent even tho a considerable portion of the nitro naphthalene precipitated when the ether solution was added to the ammonia. The solution exhibited the same colors as nitro benzene and nitro toluene only to a lesser extent probably due to its being more difficultly soluble. As in the case of nitro ben-

zene and toluene complete reduction would proceed according to the following equation:

$$\text{Alpha } C_{10}H_7NO_2 + 6Na + 6NH_3 + 6NH_4Cl =$$
$$\text{Alpha } C_{10}H_7NH_2 + 6NaCl + 12NH_3 + 2H_2O$$

Five grams of alpha nitro napthalene was dissolved in ether and this solution added to 150 c.c. of liquid ammonia containing ten grams of ammonium chloride. Five grams of sodium was then added to the mixture.

A very interesting and unusual phenomenon accompanied the addition of the slices of metallic sodium. The entire surface of the sodium exposed to the solution glowed with a beautiful greenish yellow light. In the dark, the whole Dewar bulb glowed as if filled with some phosphorescent substance and a considerable amount of light was given off. The reaction did not appear to be any more vigorous or to evolve any more heat than similar reactions with nitro benzene and toluene. The sodium continued to give off this light until all the nitro napthalene had been used up. Small portions of sodium were dissolved in ammonia and lumps of nitro napthalene were added. These glowed with the same color as the sodium in the former case and the points of phosphorescent light dancing about in a blue background was quite beautiful. Apparently this is merely another example of the phenomena known as chemilumenesence but was characterized by the large amount of light given off. The light more nearly resembled that of the glow worm

in appearance.

It would be very interesting to try other napthalene derivatives and especially beta nitro napthalene.

The mixture resulting from the reduction was usually a very viscous oily liquid which would not crystallize. Addition of hydrochloric acid and acetyl chloride seemed to form some compound but it was so impure as to be worthless in identification. The mixture resulting from the reduction was extracted with ether and the ether was evaporated. The oil was then distilled and boiled at approximately 280°. The distillate solidified to a light brown substance having a melting point of 45-48°. This compound was treated with acetyl chloride and the substance formed from this reaction melted at 157°. A sample of alpha acetnapthalid was prepared which melted at 159°. A mixture of the known and unknown substances melted at 158°. From these data, the substance was evidently alpha napthyl amine.

Five grams of nitro napthalene yielded about five grams of the thick tarry oil which, on distillation, yielded about three grams of napthylamine, the remainder in the distilling flask being a tarry substance.

In acid (NH_4Cl) solution then, alpha nitro napthalene is reduced to alpha napthyl amine; a reaction one would expect from the behavior of the preceeding aromatic nitro compounds.

Benzaldehyde.

Benzaldehyde dissolves in ammonia with a colorless to light yellow solution depending upon the purity of the benzaldehyde. It was thought that benzaldehyde might reduce to benzyl alcohol according to the following equation:

$$C_6H_5CH_2 + 2Na + 2NH_3 + 2NH_4Cl = C_6H_5CH_2OH + 2NaCl + 4NH_3$$

Ten grams of benzaldehyde was dissolved in 150 c.c. of ammonia containing eleven grams of ammonium chloride. Five grams of sodium was added and the reaction proceeded quietly and rapidly. The ammonia was evaporated and water was added to the mixture. A yellow oil separated which consisted of a mixture of some unchanged benazldehyde with some other substance. Hydrochloric acid was added to the oil which at once changed to a solid. This solid, on treatment with sodium hydroxide, changed back to the oil. A portion of the solid substance was recrystallized from water and melted at 257° and evidently was the salt of an amine.

Samples of the solid salt were weighed and titrated with standard sodium hydroxide. On the assumption that one mole of hydrochloric acid was combined with one mole of the amine, the molar weight was calculated to be 233.5. The oil or amine was insoluble in water and its benzoyl derivative melted at 108 - 110°. From these data, the compound was evidently di-benzyl amine. The water solution remaining after the separation of the insoluble oil contained no benzyl amine. The low melting point of the ben-

zoyl derivative of the di benzyl amine 108-110° as against 112° was probably due to some impurity.

Ten grams of benzaldehyde yielded usually about three grams of di-benzyl amine.

Then, in acid solution, benzaldehyde yields di benzyl amine according to the following equation:

$$2C_6H_5CHO + 4Na + 4NH_3 + 4NH_4Cl =$$
$$(C_6H_5CH_2)_2NH + 4NaCl + 2H_2O + 7NH_3$$

Some benzaldehyde remained unchanged after reduction. No benzyl alcohol was recovered from the reaction. Thinking that the reaction might take place with the preliminary formation of hydrobenzamide some of this substance was placed in ammonia and sodium added but no reduction seemed to take place and all the hydro benzamide was recovered unchanged. This reaction should be investigated further as it seems there should be some benzyl amine formed as well as some benzyl alcohol.

Cinnamic Aldehyde.

Cinnamic aldehyde dissolves readily in liquid ammonia forming a colorless solution. The solution reacts vigorously with sodium without any change in color. Since no amine was formed, reduction probably took place according to the following equation:

$$C_6H_5CH : CH - CHO + 2Na + 2NH_3 + 2NH_4Cl =$$
$$C_6H_5CH : CH - CHO + 2NaCl + 4NH_3$$

To a solution of nine grams of ammonium chloride dissolved in liquid ammonia was added ten grams of cinnamic

aldehyde followed by four grams of sodium. After reduction, the ammonia was evaporated and water was added in sufficient quantity to dissolve the sodium and ammonium chlorides remaining. A light yellow oil separated whose odor differed from that of the aldehyde. This oil on treatment with benzoyl chloride gave a compound which melted at 119°. A sample of cinnamyl alcohol was treated with benzoyl chloride and a compound melting at 119° was obtained. A mixed melting point of this compound with the unknown melted at 119°. Evidently the cinnamic aldehyde was reduced to cinnamyl alcohol.

Then, in acid (NH_4Cl) solution, cinnamic aldehyde is reduced to cinnamyl alcohol with sodium in liquid ammonia.

Benzal Aniline.

Benzal aniline was dissolved in ether and this solution added to liquid ammonia containing ammonium chloride. The solution which was colored from the more or less impure benzal aniline became colorless after addition of the sodium. The reaction may proceed according to the following equation:

$$C_6H_5CH = N - C_6H_5 + 2Na + 2NH_3 + 2NH_4Cl =$$

$$C_6H_5CH_2 - NH - C_6H_5 + 2NaCl + 4NH_3$$

To 150 c.c. of liquid ammonia containing twelve grams of ammonium chloride was added ten grams of benzal aniline dissolved in ether. Six grams of sodium was added and the solution became colorless. The reaction proceeded quietly.

The ammonia was evaporated and water was added. A brown oil separated. This oil formed a salt with hydrochloric acid which was difficultly soluble in water and melted at 197°. A portion of the oil was treated with benzoyl chloride which gave a compound melting at 102-103°. From the above, it would seem that the benzol aniline is reduced to benzyl aniline by the action of sodium in liquid ammonia.

Anis Alcohol.

Anis alcohol is readily soluble in ammonia and reacts vigorously with the added sodium. The solution remains colorless. The reduction probably takes place for the formation of the alcohol according to the following equation:

$$CH_3OC_6H_4CHO + 2Na + 2NH_3 + 2NH_4Cl =$$

$$CH_3OC_6H_4CH_2OH + 2NaCl + 4NH_3$$

Fifteen grams of anis aldehyde was dissolved in 150 c.c. of ammonia containing eleven grams of ammonium chloride and five grams of sodium was added. The reaction proceeded vigorously. After evaporation of the ammonia, the mixture was extracted with ether and this solution dried. The ether was distilled off and the remaining yellow oil boiled at 240° - 260°. The oil was not an amine. The oil was probably anis alcohol but at the time of this writing had not yet been identified.

GENERAL CONCLUSIONS.

Sodium dissolved in ammonia is a strong reducing agent and the addition of ammonium chloride gives the effect of reduction in acid solution. The reactions seem to take place smoothly and rapidly. The reduction appears to take place as rapidly as ionic reactions take place in water. They differ in this respect from other organic reactions which take considerable time.

Liquid ammonia and sodium furnish a fairly strong and not inconvenient method for the reduction of organic compounds. Compounds which might ordinarily be unstable are stable at the temperature of liquid ammonia.

As yet, not a great many reactions in liquid ammonia with sodium have been tried but from what is known it appears that the reduction products are those which one would expect from reduction as ordinarily carried out. This subject offers a very interesting field of investigation.

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